Groundwater Sulfate Reduction Plan

Minntac Tailings Basin

Prepared for
U. S. Steel Minntac

July 2013
Revised January 2014

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1.0 Introduction

1.1 Groundwater Sulfate Reduction Plan Objective

This Groundwater Sulfate Reduction Plan (Plan) has been prepared to comply with the Minnesota Pollution Control Agency (MPCA) Schedule of Compliance (SOC) Amendment Number 1 signed by the MPCA and United States Steel Corporation (U. S. Steel), which went into effect February 12, 2013. This Plan has been prepared in accordance with the requirements of the amendment, which specify the evaluation of additional methods for reducing sulfate concentrations within the facility's tailings basin beyond what was described in U. S. Steel's Dry Control Effectiveness Report (U. S. Steel, 2012), and/or installing measures to reduce sulfate concentrations in groundwater prior to migration beyond the Facility's current property boundary. The ultimate goal of remedial actions, as defined in the SOC is to reduce sulfate concentrations to below 250 milligrams per liter (mg/L) in groundwater at the property boundary near monitoring well MW12. A site map showing the eastern side of the U. S. Steel Minntac tailings basin is included as Figure 1. Amendment No. 1 of the SOC requires that a groundwater sulfate reduction plan be submitted to the MPCA within 150 days of the effective date. This Plan presents results of a preliminary alternatives evaluation, proposed actions for additional data collection to better assess likely sulfate reduction alternatives, and a preliminary schedule for achieving the requirements outlined in SOC Amendment No. 1.

1.2 Plan Organization

This report includes the following sections:

Section 1 – Introduction

Section 2 – Background

Section 3 – Alternatives Screening

Section 4 – Additional Data Needs

Section 5 – Remedy Implementation

Section 6 – Schedule

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2.0 Background and Historical Data

2.1 U. S. Steel Minntac Operations and Tailings Basin Description

The following information is taken from the Facility Description contained in the NPDES/SDS permit for the U. S. Steel Minntac tailings basin. The Minntac tailings basin facility is regulated by NPDES Permit No. MN0057207 and includes a tailings basin, the drainage areas contributing surface water runoff to the tailings basin, a wastewater treatment plant, wood processing facility, petroleum fuel storage area and a plant site reservoir.

The principal activity at this facility is taconite processing. At the maximum operating rate planned during the life of this permit, the facility will generate 16.5 million long tons (LT) of taconite pellets per year.

The Minntac taconite processing plant includes a series of crusher and screens, a crusher thickener, a concentrator, agglomerators and various auxiliary facilities. The concentrator uses a series of mills, magnetic separators, classifiers, hydrocyclones, screens and thickeners, and a flotation process to remove waste silica to produce taconite concentrate. Concentrate is delivered to the agglomerator in slurry form to be converted into either standard or fluxed pellets. Concentrate slurry is mixed with a combination of limestone dolomite (fluxstone) for the production of fluxed pellets, while standard pellets contain no fluxstone additive. The concentrate slurry, either fluxed or standard, is subsequently dewatered using disc filters. The filter cake is then mixed with bentonite and formed into greenballs in balling drums. The greenballs are dried, heated, and fired in a grate kiln to make pellets. The pellets are then cooled and then loaded for rail transport.

The wastewater discharges to the tailings basin are comprised of the following, with estimated average flow rates (if known):

- Fine tailings slurry/concentrator process water (15,700 gallons per minute -gpm).
- Agglomerator process water (1,700 gpm).
- Wastewater treatment plant discharge (40 gpm).
- Laboratory wastewater (3,650 gallons per year).
- Plant non-process water (wet scrubber discharge, floor wash, roof water runoff, non-contact cooling water – 16,700 gpm).
- Runoff from plant area, stockpile areas.

An average of 26.5 million LT of dry fine tailings and 12.5 million LT of coarse tailings are disposed of in the tailings basin each year. Coarse tailings are generated from a classifier, following the first stage of milling and magnetic separation. Fine tailings are generated from the crusher thickener overflow and concentrator thickener underflow. The fine tailings slurry and concentrator process water is discharged by gravity flow through pipes from the Step I, II, and III concentrator thickeners to a series of open ditches to the tailings basin. The discharge from the flotation process is restricted to the Step I thickener effluent pipe. The tailings basin is segmented into several cells for dust management purposes. The fine tailings slurry is periodically diverted from one cell to another.

A large portion of the water contained in the fine tailings slurry returns to the 1,400-acre tailings basin clear water reservoir after the slurry solids have dropped out in the tailings basin fine tailings cells. A permanent pumping station located on the south side of the tailings basin reservoir returns water to the plant site reservoir for reuse in the process.

The various basin cells are separated by dikes, each constructed with a single berm of coarse tailings placed by truck and other forms of auxiliary equipment. Most of the perimeter dam for the tailings basin is constructed with a fine tailings core placed between parallel inner and outer coarse tailings dikes. That part of the perimeter dam on the southwest side of the basin is constructed in the same manner as the interior dikes. The tailings basin is sited on an area of glacial and glaciofluvial deposits, which are principally sand, gravel and glacial till.

The Minntac tailings basin is positioned at a location that straddles the drainage divide between the Dark River and Sand River watersheds. Discrete surface seepage areas have been identified along the toe of the perimeter dike on the east and west sides of the tailings basin that report to one of these watersheds. Most of the north side and all of the west side of the tailings basin perimeter dike is located in the Dark River Watershed. One of the largest westerly surface seepage points exists at the headwaters of the Dark River and is monitored as required by NPDES/SDS Permit No. MN0057207. All of the surface seepage and a portion of the shallow groundwater seepage that previously reported to the Sand River Watershed is collected for reuse by a seepage collection and return system (SC&R) that was installed by U. S. Steel in 2010 and became fully operational in June 2011.

2.2 Current Conditions

Current ground conditions near MW12 include a large wetland, surrounded by forested uplands. The subsurface geology near MW12 begins with peat deposits to depths of up to 8.5 feet below ground surface (bgs). The peat is underlain by a 3.5 foot thick layer of clay. Sand and gravel with various amounts of gravel and boulders are present below the clay. This sand and gravel zone extends to bedrock which is approximately 29.5 feet bgs. Two cross sections have been created to show the subsurface conditions. Cross Section A-A' shown on Figure 3 is a generally north-south cross section perpendicular to groundwater flow. Cross Section B-B' shown of Figure 4 is an east-west cross section that runs parallel with groundwater flow.

Hydraulic conductivity testing was completed at MW12 in 2012 (CRA, 2012). The average hydraulic conductivity was determined to be 0.003 feet per minute which, when combined with the local hydraulic gradient (0.003) and an effective porosity of 0.1 typical of the glacial overburden in that area, equates to a groundwater velocity of approximately 50 feet per year.

Sheet pile was installed as part of the SC&R at each discrete surface seepage location to prevent dewatering of downgradient wetlands and promote additional subsurface seepage capture. The location of the sheet pile in the subject area is shown on Figure 2. Records indicate that the sheet pile was advanced to a depth of 13 – 14 feet bgs. Based upon a review of the pumping tests, groundwater flow below the approximate 400-foot length of installed sheet pile is estimated to be approximately 26 gallons per minute (gpm).

Sulfate concentrations have been periodically monitored in on-site piezometers PZ5S, PZ5D and off-site piezometers PZ4S, PZ4D, PZ6S, PZ6D, PZ7S, and PZ7D (Figure 2), since 2010. Sulfate concentrations ranged from 529 to 748 mg/L in the on-site piezometers and from 7.6 to 22.6 mg/L in the off-site wells (see Table 1 below). In response to MPCA requirements, U. S. Steel installed a piezometer nest (PZ12S, PZ12I and PZ12D) in 2012 to monitor sulfate concentrations near the U. S. Steel facility property line off the northeast corner of the Minntac tailings basin (also shown on Figure 2). Sulfate concentrations in the PZ12 piezometer nest ranged from 460 to 577 mg/L in 2012. PZ12D now serves as MW12 for the purpose of routine sampling required during April, July and October, in conjunction with sampling from a series of monitoring wells installed around the tailings basin perimeter dike in 1981. Sulfate concentrations in MW12 are assumed to be representative of concentrations at the adjacent U. S. Steel property line slightly downgradient. Samples collected from PZ12D from three separate sampling events in 2012 showed sulfate ranging from 460 to 476 mg/L, while samples collected from MW12 in 2013 showed sulfate at 385 to 420 mg/L. This would suggest that sulfate concentrations at the U. S. Steel property boundary near MW12 are decreasing, most likely due to operation of the SC&R.

2.3 Site Conceptual Model

Based upon a review of the existing data and the *Subsurface Exploration and Seepage Evaluation* prepared by STS (STS, 2007), water from the tailings basin is seeping from the Minntac tailings basin perimeter dike at a rate of 0.17 cubic feet per second (cfs) per every 1,000 feet of dam length. For the project area, seepage through approximately 400 lineal feet of perimeter dike length is assumed to be contributing to the elevated sulfate concentrations observed at MW12. The 400-foot length of perimeter dike equates to an approximate flow of 0.07 cfs (31.5 gpm). This flow rate correlates with the approximately 26 gpm flow estimated from hydraulic conductivity testing conducted on the PZ12 piezometer nest in 2012 (CRA, 2012).

The sulfate concentration in water within the pool of the tailings basin is approximately 950 mg/L. Through the processes of dilution from natural groundwater flow and natural attenuation, the sulfate concentration observed at the PZ12 piezometer nest is reduced to the ranges shown above, which exceeds the 250 mg/L groundwater standard applicable at the property line. Groundwater monitoring results from off-site wells have shown sulfate concentrations one to two orders of magnitude below what was observed on-site in MW12 and are shown on Table 1.

Table 1– Sulfate Concentrations in Groundwater (all results in mg/L).

Well Name	Location	Round 1 (8/19/2010)	Round 2 (8/26/2010)	Round 3 (9/30/10)	Round 4 (4/10/12)	Round 5 (5/7/12)	Round 6 (6/6/13)
PZ4S	Off-site	7.6	7.9	NS	11.5	NS	NS
PZ4D	Off-site	10.8	10.1	NS	8.8	NS	NS
PZ5S	On-site	529	569	572	852	NS	NS
PZ5D	On-site	672	674	639	748	NS	735
PZ6S	Off-site	12.7	12.0	8.0	10.2	NS	NS
PZ6D	Off-site	22.6	18.4	17.7	16.5	NS	NS
PZ7S	Off-site	9.4	8.7	9.0	21.9	NS	NS
PZ7D	Off-site	9.1	8.6	8.8	9.5	NS	NS
PZ12S	On-site	-	-	-	577	562	NS
PZ12I	On-site	-	-	-	564	545	NS
PZ12D /MW12	On-site	-	-	-	466	460 (476 on 5/15/12)	420 (385 on 5/31/13)

NS – Not Sampled
- – Well not installed

As shown on Figure 2, the off-site piezometers (PZ4, PZ6, and PZ7) are installed at or near the edge of the east-west trending wetland channel, and may be on the periphery of the sulfate-influenced groundwater flow leaving U. S. Steel property.

3.0 Alternatives Screening

As part of the initial planning for work to be completed under this plan, various alternatives were screened with respect to implementability, effectiveness and costs. Appendix A contains a table showing the various alternatives that were evaluated, along with a preliminary description of each alternative; the associated advantages and disadvantages; an assessment as to the effectiveness, implementability, and cost; and an assessment of additional data needs required to fully evaluate each alternative. The data gaps section of the table presented in Appendix A provides the basis for additional data collection and evaluation activities outlined in this plan. Section 3.1 below provides a brief description of the alternatives. Section 3.2 provides a summary of the alternatives selected to meet plan objectives.

3.1 Alternatives Description

Remedial alternatives considered to meet the objectives outlined in this plan were separated into eight categories. The eight major alternatives are as follows:

- Baseline – No Action,
- Source Mitigation – Currently Planned,
- Source Mitigation – Prevent Oxidation of Tailings,
- Hydraulic Containment – Active,
- Hydraulic Barrier – Passive,
- Hydraulic Containment – Hybrid
- Sulfate Treatment – In-Situ bio-chemical reduction, and
- Sulfate Treatment – Active hydraulic containment with ex-situ treatment.

These eight categories are further sub-divided into variations of the remedial action. The baseline alternative was assumed to be no action; however, based on U. S. Steel's current knowledge, it is unlikely that compliance with the sulfate standard at the property boundary will ever be achieved with this alternative. Furthermore, the no-action alternative does not meet all requirements contained in SOC Amendment No. 1. The currently planned source mitigation alternative included the dry controls currently planned for implementation and summarized in the Dry Controls Effectiveness Report (U. S. Steel, 2012). Other alternatives that were considered are summarized below.

3.1.1 Source Mitigation – Prevent Oxidation of Tailings

Additional methods for reducing sulfate concentrations within the facility's tailings basin beyond what was described in U. S. Steel's Dry Control Effectiveness Report include alternatives aimed at reducing or preventing the formation of sulfate via tailings oxidation within the basin. Tailings oxidation is a recognized source of sulfate within the Minntac process water system. Based off of 40 years worth of site data and modeling, an estimated 20 – 25% of the sulfate load of the process water is attributable to the oxidation of tailings in the basin. This alternative would include the assessment and potential mitigation of sulfate within the tailings basin and surrounding areas. However, since the stated goal of SOC Amendment No. 1 is to re-establish compliance with the groundwater sulfate standard at the Facility's property boundary as soon as possible, mitigation of tailings oxidation is not considered to be a feasible alternative for this compliance issue. The more focused approaches provide a much higher probability of achieving compliance within a shorter time frame and the potential for success of the focused approaches can be measured much more easily.

3.1.2 Hydraulic Containment – Active

Active hydraulic containment will attain the sulfate reduction goals at the property line near MW12 through mechanical extraction of impacted groundwater. Mechanical extraction of groundwater can be achieved through installation of an extraction well network or through installation of a horizontal drain and associated sumps and pumps. Either method will work on the same principal; intercepting sulfate affected groundwater, and/or pumping water from the unconsolidated aquifer, and then pumping the intercepted groundwater back into the U. S. Steel tailings basin.

3.1.3 Hydraulic Barrier - Passive

The hydraulic barrier alternative would include constructing a hydraulic barrier downgradient of the tailings basin perimeter dike that will significantly reduce groundwater flow from the tailings basin. This alternative includes three options; a) sheet pile wall, b) slurry wall or c) grout injection into the subsurface. Effectiveness of these different options would require a connection to the bedrock underlying the unconsolidated aquifer, and would need to be constructed to a sufficient length to stop water from flowing around the hydraulic barrier to the property boundary near MW12.

3.1.4 Hydraulic Containment – Hybrid

The hybrid hydraulic containment alternative would include constructing a passive hydraulic barrier as described in Section 3.1.2 above, supplemented by the active hydraulic containment alternative described in Section 3.1.1. This alternative would potentially improve the effectiveness of both the active hydraulic containment and passive hydraulic barrier alternatives. Downgradient wetland effects and pumping rates could potentially be reduced with this alternative in comparison to a system that strictly uses active hydraulic containment.

3.1.5 Sulfate Reduction - In-Situ Bio-chemical Sulfate Reduction

In-situ bio-chemical sulfate reduction would reduce sulfate concentrations in the groundwater near MW12 by augmenting and/or enhancing the groundwater conditions to increase sulfate reducing bacteria (SRB) activity. A description of sulfate reduction in general and specifically by SRB is included as Appendix B. Three implementation options were screened for this alternative. These included: a) excavating a trench perpendicular to groundwater flow that could be filled with a mix of granular zero valent iron (ZVI), mulch and/or additional substrates to create reducing conditions and feed the SRB; b) injecting (batch injection or continuous dosing) a suitable carbon substrate (potentially mixed with ZVI) into permanent wells installed in the unconsolidated aquifer on U. S. Steel property; or c) injecting a suitable carbon substrate (potentially mixed with ZVI) into temporary wells or direct push injection borings on U. S. Steel property.

3.1.6 Sulfate Reduction –Active Hydraulic Containment with Ex-Situ Treatment

This alternative would use groundwater extraction as described in Section 3.1.1 above. However, this alternative would also include ex-situ treatment of groundwater to remove sulfate, potentially with subsequent re-injection re-release of treated water to mitigate resulting wetland or hydrologic disruptions caused by extraction alone, or to reduce the time to reach compliance at MW12. Two methods of ex-situ treatment screened as part of the alternatives analysis included a) reverse osmosis (RO) or b) ion exchange (IX) technologies. For purposes of this alternatives screening, a stand-alone RO or IX treatment system would be considered for this area.

3.2 Alternatives Selected to meet Plan Objectives

Based on the alternative screening presented in Appendix A and summarized in this section, U. S. Steel will pursue active or hybrid hydraulic containment with or without ex-situ treatment and in-situ sulfate reduction as potential avenues for achieving compliance with Amendment No. 1 to the SOC.

At the time Amendment No. 1 to the SOC was finalized, the SC&R had eliminated all surface discharges reporting to the Sand River Watershed, and sulfate in groundwater at the Minntac property boundary at concentrations over the state standard was the only outstanding compliance issue on the east side of the tailings basin. Based on NPDES permit renewal discussions with MPCA, it may be determined that the tailings basin is an NPDES point source due to deep seepage and subsequent seepage daylighting, and would therefore be subject to applicable surface water quality standards.

As this determination may not be finalized until a permit is reissued for the basin, the final alternative for compliance with SOC Amendment No. 1 via the Plan is still unknown. The final remedy will be chosen based on the feasibility of the alternative to achieve compliance with the groundwater sulfate standard at the property boundary, and also to address other requirements on the east side of the Minntac tailings basin if MPCA determines that deep seepage from the tailings basin will be classified as a point source discharge.

Because the timeline for MPCA to reissue the Final Tailings Basin NPDES Permit is unknown, U. S. Steel will begin implementation of this Plan upon MPCA approval. However, U. S. Steel will take into consideration any regulatory or site-specific changes which may occur during the implementation of the Plan and will chose a final alternative for compliance with SOC Amendment No. 1 which will most effectively be integrated into an overall facility compliance strategy.

4.0 Additional Data Needs

4.1 Additional Data Needs

Through the alternatives screening process, additional data requirements were identified that may need to be addressed for successful implementation of the selected alternatives listed in Section 3.2. Potential data requirements may include: 1) additional groundwater flow model data and 2) a microcosm study. An overview of potential data requirements and data collection actions designed to meet these requirements needs is listed below.

Data quality objectives were determined for each data set that may be generated during investigation of the selected alternatives. The following data collection activities will be considered:

- Sample locations and depths;
- Observations of subsurface conditions;
- Concentrations of sulfate and other water quality parameters in groundwater;
- Water level measurements;
- Measured aquifer responses to pumping and other hydraulic stresses, and
- Changes in sulfate and other groundwater quality parameters in response to additives used to stimulate bio-chemical activities.

Any additional sample locations and depths will need to be documented with sufficient accuracy so they can be located during data review and analysis. The sampling design needs to represent the local conditions of interest for the purposes of remedial action planning. Observations of subsurface conditions need to be accurate and complete.

The chemical concentration data need to be sufficiently precise, accurate, representative, and complete so as to allow a meaningful comparison to applicable standards. Acceptable criteria for precision and accuracy are provided by the analytical laboratory and will include acceptable ranges for laboratory control sample recovery and surrogate recovery. Representativeness will be evaluated in relation to blank sample results. Comparability will be addressed by utilizing procedures and methods described in this plan, which incorporates standard sampling and analytical methods. Samples will be submitted for analysis to Pace Analytical, Inc., Virginia, MN, to ensure accuracy of results and proper quality assurance/quality control procedures are followed.

Water level measurements, including in response to aquifer testing, will be measured within 0.01 feet, referenced from the top of the temporary wells and in turn referenced to top of a nearby control point. This will allow calculation of hydraulic gradients, interpretation of the groundwater flow direction, and an estimation of hydraulic conductivity.

The measurements of screening parameters in groundwater samples need to be sufficiently accurate to help assure the collection of representative groundwater samples used for evaluating effectiveness of the remedial alternatives.

4.2 Groundwater Flow Model

A three-dimensional groundwater flow model will be used to assess the effectiveness and timing of compliance for active hydraulic containment. Parameters such as groundwater flow velocity, travel time, impacts to downgradient wetlands, basic groundwater field parameters (dissolved oxygen, pH, and specific conductance), as well as sulfate concentrations, will need to be evaluated with respect to the baseline condition and potential alternative actions. The groundwater flow model will allow analysis and comparison of the relationship between various cause and effect attributes of the selected alternatives, such as: groundwater extraction rates, well spacing requirements, time required to achieve compliance with the requirements of Amendment No. 1 to the SOC, etc.

The MODFLOW model recently constructed for the east side of the tailings basin and that portion of the Sand River Watershed encompassing the Twin Lakes will be evaluated for its applicability to this effort. Additional field data collection may be required to properly calibrate and operate the groundwater flow model. These additional field data requirements may include a higher density of borings near the point of compliance to determine subsurface stratigraphy/soil characteristics, longer-term hydraulic conductivity testing to determine groundwater flow parameters and boundary conditions, and longer term water level monitoring to assess the connectivity of the unconsolidated aquifer to the downgradient wetlands.

4.3 Microcosm Study

In order to assess and optimize the in situ bio-chemical reduction of sulfate, additional groundwater sampling and a microcosm study may be conducted. Groundwater sampling of existing wells/piezometers in the subject area, e.g., the PZ5 and PZ12 nested piezometers, would be used to assess existing groundwater parameters such as DO, oxidation reduction potential (ORP), specific conductance and other parameters key to ensuring SRB have the proper conditions to live and thrive. Table 2 shows the full list of parameters that would likely be analyzed to evaluate the condition of the groundwater. The need for additional monitoring wells will be assessed following initial sampling and analysis.

Table 2 – Groundwater Sampling Parameters

Parameter	Method
Dissolved Oxygen	YSI/Field Meter
Temperature	YSI/Field Meter
ORP	YSI/Field Meter
Specific Conductance	YSI/Field Meter
pH (field)	YSI/Field Meter
Biochemical Oxygen Demand	SM 5210B
Chemical Oxygen Demand	SM 5220D
Nitrogen, Nitrate + Nitrite	EPA 353.2 or Field Photometer
Phosphorus, Total	EPA 365.1 or Field Photometer
Sulfate	EPA 300.0
Calcium, Total	EPA 200.7 or Field Titration
Iron, Total	EPA 200.7 or Field Photometer
Iron, Dissolved	EPA 200.7 or Field Photometer
Magnesium, Total	EPA 200.7 or Field Titration
Solids, Total Dissolved	SM 2540C or Field Meter
Carbon, Total Organic	SM 5310 C-00 or Field Photometer
Major Cations and Anions	EPA 200.7 or 300.0
Manganese, Total	EPA 200.8 or Field Photometer
Manganese, Dissolved	EPA 200.8 or Field Photometer

Following initial groundwater sampling, a microcosm study would be completed on water extracted from on-site wells to determine effectiveness of various carbon substrate/ZVI combinations for use as part of an in situ bio-chemical sulfate reduction operation. This operation could be used to replace active hydraulic containment if testing demonstrates that this approach is both effective and economical in comparison to active containment.

4.3.1 Objectives

The objectives of a microcosm study in advance of either potential pilot testing or a full-scale design and installation of an in-situ bio-chemical remedy include the following:

- Determine what treatment efficiencies can be achieved with the site-specific physical and chemical conditions.

- Evaluate a variety of substrate and energy sources to identify an acceptable range of components that will meet the treatment criteria.

- Identify potential long-term performance issues (hydraulic conductivity, treatment efficiency) and use the information to develop a more detailed in-situ bio-chemical design.

Microcosm testing can be used to develop some of the basic parameters including a range of effective substrate combinations and the likely residence times required for the selected media. Pilot testing would be needed to evaluate treatment within 'field' conditions to identify potential design issues related to installation of full-scale treatment and the potential for hydraulic issues (for example, leakage under or around the in situ bio-chemical treatment technique selected, such as a permeable reactive barrier (PRB), or fouling due to chemical or biological precipitation).

4.3.2 Proposed Scope and Methods

Sealed microcosm vials would be used to evaluate the potential effectiveness of chemical additions for sulfate reduction. A total of three chemical additions would be evaluated over a time series of up to one month using a series of sacrificial microcosm vials. Details of the final set-up may be revised based on the results of the additional site characterization activities described in the previous section, however, the likely experimental set-up for this test will include:

- Three sets of sealed (~140 ml) serum vials filled with 10 grams of aquifer sediment (collected during boring installation) and approximately 100 ml of aquifer water containing sulfate. Material added to the three sets of vials will be:
    - 1 gram EHC® (approximately 10 percent by weight ratio to the aquifer sediments)
    - 10 mL water soluble carbon substrate.(approximately 10 percent of the aquifer water)
    - 10 mL emulsified oil carbon substrate with approximately 20% ZVI. (approximately 10 percent of the aquifer water)
- Each set will include duplicate bottles to be sacrificed for analysis of sulfate and other parameters of interest on the following days: 0 (baseline), 2 days, 4 days, 7 days, 14 days, 21 days, and 28 days.

Vials will be set-up in an anaerobic box and purged of any oxygen at the beginning of the tests. Vials will be sacrificed on the days listed and analyzed primarily for sulfate. Tests will be stopped at the end of 28 days or if the results of the analysis show that the sulfate concentration is less than 100 mg/L (or 20 percent of the initial value, whichever is lower) after any of the proposed sampling dates.

4.4 Ex-Situ Treatment Investigation

A novel ion-exchange technology, being developed by FB Water Treatment, may be investigated as a potential treatment option for groundwater that is collected as part of an active hydraulic containment system.

The treatment technology would be evaluated to determine the effectiveness of treatment for overall sulfate reductions prior to returning the recovered water back to the tailings basin, subsequent reinjection of treated water to mitigate resulting wetland or hydrologic disruptions caused by extraction alone, reinjection of treated water near MW12 to reduce the time to reach compliance at the property boundary, or release of treated water to downstream surface waters.

Applicability of the FB Water Treatment technology will first be evaluated via demonstration-scale testing on a small batch of tailings basin return water (e.g., 100 gallons), representative of seepage to the Sand River Watershed. Results of the demonstration testing will determine the next stage of testing that will be pursued. Successful demonstration will likely lead to on-site pilot-scale testing at Minntac.

4.5 Reporting and Design

Results from the data collection field activities, microcosm study and ex-situ treatment investigation will be validated and reviewed for consistency with the data quality objectives. This information will help to define the path forward in selecting the best alternative to achieve compliance with applicable water quality standards. Following an evaluation of the existing groundwater flow model, any additional field data deemed necessary to supplement the model will be developed and incorporated. The model would then be ready for use in design support of the chosen alternative. A design report outlining the configuration of any system selected for full-scale implementation will be submitted to the MPCA for review and approval.

5.0 Remedy Implementation

The remedy that will be installed and operated to achieve compliance with Amendment No. 1 of the SOC will be completed in accordance with the design report described in Section 4.

The implementation of this remedy cannot be described fully at this time but may include:

- Installation of one or more pumping wells or a groundwater drainage system,
- Installation of a hydraulic barrier wall,
- Installation of permanent power supply and discharge lines to and from the collection system, and
- Installation of controls and monitoring equipment to evaluate system performance and demonstrate compliance.

Pilot testing of ex situ treatment technologies and in situ bio-chemical sulfate reduction may also be implemented concurrent with or in place of the installation of the active hydraulic containment system, if preliminary testing provides favorable results and the initial economic analysis suggests that this may be more cost effective over the longer term.

The final remedy will be chosen based on the feasibility of the alternative to achieve compliance with the groundwater sulfate standard at the property boundary, and also to address other requirements on the east side of the Minntac tailings basin if MPCA determines deep seepage from the tailings basin will be classified as a point source discharge.

Implementation of the remedy will be documented in a construction documentation report, and a field scale/pilot test report, if necessary.

6.0 Schedule

A preliminary schedule of milestones for additional data collection, groundwater model evaluation and refinement, completion of alternatives evaluation, and subsequent design and installation of a final remedy is shown below. This schedule is the best estimate based off of known information at this time and should not be interpreted as a compliance schedule. Many factors could significantly alter this schedule. The schedule is dependent on regulatory review and any necessary site permitting (modification of existing permits or new permits) required for installations and future operation, and may change based on seasonal field restrictions and the results of the testing. The preliminary schedule shown below is subject to change:

Step	Estimated Date of Completion
1. Submittal of Plan to the MPCA	July 12, 2103
2. MPCA review	January 3, 2014
3. Submittal of Revised Plan to the MCPA	January 31, 2014
4. MPCA approval of Plan	To Be Determined
5. Selection of alternative(s) to continue investigating	2 months after Step 4
6. Determine additional data needs	6 months after Step 5
7. Hydraulic Modeling / Microcosm study	6 months after Step 6
8. Pilot study design for selected alternative(s)	4 months after Step 7
9. Pilot study permitting	To Be Determined
10. Pilot study for selected alternative(s)	1 year after Step 9
11. Evaluation of pilot study results. If pilot study findings are determined inadequate, proceed to Step 5.	2 months after Step 10
12. Submit Design of Final Remedy to MPCA	6 months after Step 10
13. MPCA Review and Approval	To Be Determined
14. Final remedy permitting	To Be Determined
15. Final remedy implementation	6 construction months after receiving all permits and agency approvals
16. Attain sulfate goal of 250 mg/L at property line	2025*

*This final date of compliance is contingent upon factors, including but not limited to, the following: time to obtain all required permits without appeal or litigation, multi-media and multi-pollutant impacts, technical and economic feasibility, and changes to the plan as a result of changes or additions to the regulatory requirements.

The estimated date for compliance with the goals of Amendment No. 1 to the SOC (milestone item No. 16) will be calculated using modeling techniques and will be verified based on pilot study results and final design parameters. Initial estimates indicate that implementation of the potential remedies chosen in this plan could take between 6 and 12 months depending upon the timing of receipt of all permits. It is estimated that the sulfate goal of 250 mg/L at the property boundary near MW12 should occur in 2025. This date is contingent on several factors, including but not limited to: the time to obtain all required permits without appeal or litigation, multi-media and multi-pollutant impacts, technical and economic feasibility, and changes to the plan as a result of changes or additions to the regulatory requirements. This date is provided solely as an estimate of the final date of compliance and may change based on modeling and pilot study results, final design parameters, permitting and approval timelines, the effectiveness of the full-scale system, and other unforeseen circumstances.

In addition to activities proposed in the Schedule, U. S. Steel will continue routine quarterly monitoring of MW12 to determine if the decreasing trend in sulfate concentrations in groundwater at the facility property boundary continues, as was observed between 2012 and 2013. It is likely that operation of the SC&R over the past 2+ years, with its corresponding removal of sulfate mass that previously reported to the wetland channel near MW12 in surface and shallow subsurface seepage, has had a positive influence on groundwater quality along the east side of the tailings basin. Consequently, the No Action alternative may result in compliance with the groundwater sulfate standard without additional remedial activities. Future groundwater monitoring should provide an indication of the overall trend of groundwater quality at the U. S. Steel property boundary near MW12 and could affect the ultimate mitigation alternative. However, U. S. Steel has no plans to rely solely on the No Action alternative to achieve compliance at the property boundary near MW12, and instead will pursue the mitigation alternative(s) identified as having the greatest potential for compliance with existing standards. Special consideration will also be given to those alternatives with broad applicability.

7.0 References

CRA, 2012. MW12D 24-Hour Pumping Test, U. S. Steel Minntac Tailings Basin, Mountain Iron, Minnesota. prepared by Conestoga-Rovers & Associates, July 9, 2012.

STS, 2007. Subsurface Exploration and Evaluation Report. Minntac Tailings Basin, Mountain Iron, Minnesota prepared for U.S. Steel by STS. November 28, 2007

U. S. Steel, 2012. Dry Controls Effectiveness Report. prepared by U. S. Steel. January, 5, 2012.

Figures

Appendix A

Technology Screening for Tailings Basin Groundwater Remediation

Appendix A
Technology Screening for
Tailings Basin Groundwater Remediation
U.S. Steel Minntac

Remedial Action	Alternative No.	Technology	Description	Advantages or Disadvantages	Screening: Effectiveness	Screening: Implementability	Screening: Data Gaps/Data Collection Requirements	Screening: Cost	Conclusion
Baseline (No Action)	1	--	The baseline alternative would be a continuation of the current operations at the site	--	The no action alternative would not be effective at reducing sulfate concentrations in groundwater at the property boundary	No remedial action would be implemented.	--	No costs are associated with this action. However, fines or other penalties would be incurred for non-compliance.	Retain as Baseline
Source Mitigation	2a	Seep collection (east and west) and dry control systems	Per the Dry Controls Effectiveness Report, source mitigation includes seep collection on the west and east sides of the tailings basin and new dry control systems installed on Lines 4-7	**Advantages**: Seep collection will decrease the volume of water leaving the tailings basin and therefore leaving the site. Dry control methods will also decrease the amount of sulfate being released into the environment. **Disadvantages**: Timeline and the tailings basin sulfate concentration will still be out of compliance, albeit much lower than at present (per Dry Controls Effectiveness Report).	Partially Effective - As stated in the Dry Controls Effectiveness Report, the proposed source mitigation is predicted to decrease sulfate concentration in the tailings basin to approximately 475 mg/L by 2032.	Currently being implemented	--	No additional costs other than already planned. Penalties will be incurred for non-compliance.	**Reject** - The alternative will not meet the sulfate concentration goal at the property line.
	2b	To be determined	Tailings oxidation is a significant recognized source of sulfate in the Minntac tailings basin. Ongoing research indicates that coarse tailings oxidation may be a significant long term source of sulfate within the tailings basin and, as a result of seepage, in surrounding surface water and groundwater. This alternative would include the assessment and potential mitigation of sulfate generated from tailings oxidation, and the relative significance of coarse tailings to the sulfate generation issue, within the tailings basin and surrounding areas.	**Advantages**: An understanding of the behavior of coarse and fine tailings and their potential as sources of sulfate would be valuable in informing any future modeling effort or evaluation of the effectiveness of proposed mitigation efforts. **Disadvantages**: U. S. Steel has not found a significant distinction between coarse and fine tailings with respect to sulfate generation due to tailings oxidation; furthermore, no technology is currently available to prevent tailings oxidation in an active disposal setting such as the Minntac tailings basin. Source reduction of this type is likely to take on the order of decades to reduce sulfate to acceptable levels in the tailings basin and those areas immediately adjacent to the tailings basin perimeter dike.	Not Effective - The assessment of tailings oxidation and potential for reduction of sulfate generation within the tailings basin would not be effective in reducing sulfate concentration in the vicinity of MW12. Mitigation strategies for this potential source of sulfate are unknown.	Partially Implementable - An assessment of the relative oxidation potential of fine vs. coarse tailings as a source of sulfate within the tailings basin could be accomplished. The assessment could likely also be used to predict the duration of sulfate generation between the two sources. The mitigation of this potential source of sulfate, and thus the implementability, is unknown.	An evaluation of the physical, chemical and mineralogical characteristics of fine tailings vs. coarse tailings would be required. Long-term bench- and pilot/demonstration-scale leaching experiments would be needed to predict sulfate generation rates and durations, as well as appropriate mitigation strategies that could be implemented into an active tailings disposal setting such as Minntac's.	Low cost to complete an assessment; mitigation costs are unknown.	**Reject** - The technology needed to prevent sulfate generation via tailings oxidation in an active tailings disposal setting such as Minntac's is unknown, and this alternative will not address compliance in a timely manner.
Hydraulic Containment - Active	3a	Horizontal drain, sumps, and pumps	A drainage trench would be excavated and aligned perpendicular to groundwater flow. Drain tile and drain rock would be installed within the trench. Sumps would be installed along the alignment containing pumps. Pumps would be installed within the sump, and associated piping will allow the system to transfer collected water to the tailings basin.	**Advantages**: Can adjust flow rate to meet groundwater flow requirements. Installation can be completed with one-pass or standard excavation equipment. **Disadvantages**: This is an active system. Continuous O&M of pumps and piping. Extended power outages or system down-time would potentially allow sulfate affected water to leave the property. Potential impacts to wetlands downgradient of hydraulic containment if pumping rates lower the water table.	Potentially Effective - This alternative has high likelihood of being successful at preventing sulfate affected water from leaving the property when the system is operational. Extended down-time may allow sulfate affected water above regulatory standards to leave the site. Wetland impacts and hydrogeology need to be further defined to ensure effectiveness. Effectiveness will be immediate upon completion of this alternative.	Potentially Implementable - Horizontal drains at depths of approximately 30 feet below ground surface (bgs) can be constructed using standard trenching or one-pass trenching techniques. Sumps and pumps can be selected to meet the range of flows anticipated from modeling. Piping and system controls can be designed to meet the climate and flow requirements of the project.	Higher resolution data on depth of bedrock, soil materials and boulder size. Groundwater flow model to evaluate effectiveness and simulate pumping conditions, evaluate sulfate concentrations at the property line under multiple pumping rates and evaluate impacts to wetlands.	Moderate capital costs and moderate annual O&M costs.	**Retain** for further analysis.
	3b	Wells and pumps	A line of wells, or multiple lines of wells will be installed to collect groundwater and pump the groundwater back to the tailings basin.	**Advantages**: Can adjust flow rate to meet groundwater flow requirements. Well installation may be lower cost and simple installation compared to 3a. **Disadvantages**: This is an active system. Continuous O&M of pumps and piping and wells will be required. Extended power outages or system down-time would potentially allow sulfate affected water to leave the property. Potential impacts to wetlands within the area.	(See Alternative 3a)	Potentially Implementable - Extraction wells installed to depths of approximately 30 feet below ground surface can be constructed using traditional drilling methods. Pumps can be selected to meet the range of flows anticipated during modeling. Piping and system controls can be designed to meet the climate and flow requirements of the project.	Higher resolution data on depth of bedrock and soil materials. Groundwater flow model to evaluate effectiveness and simulate pumping conditions, evaluate sulfate concentrations at the property line under multiple pumping rates, and evaluate impacts to wetlands.	Moderate capital costs and moderate annual O&M costs.	**Retain** for further analysis.

Remedial Action	Alternative No.	Technology	Description	Advantages or Disadvantages	Screening: Effectiveness	Screening: Implementability	Screening: Data Gaps/Data Collection Requirements	Screening: Cost	Conclusion
Hydraulic Barrier - Passive	4a	Sheet Pile	Advance sheet pile to the depth of bedrock across the area of interest.	**Advantages:** Construction would likely be simple. And if sheet pile can reach bedrock, this alternative may be effective. **Disadvantages:** Previous installation of sheet pile could not be advanced to the bedrock contact. Potential impacts to wetlands within the area caused by cutting off flow.	Potentially Effective - Should sheet pile be able to intercept the bedrock, and be located horizontally between lower permeable materials, this alternative has the potential to be effective. Full effectiveness shortly after completion of construction.	Not Implementable - Sheet pile installed in 2010 could not be advanced to bedrock. It is assumed that similar refusal would occur at the cobble/bedrock layer.	Higher resolution data on depth of bedrock and soil materials, both in the target flow zone and in surrounding upland units. This would be required to understand if water will flow around hydraulic barrier alternatives. A groundwater flow model would be required to evaluate effectiveness of alternatives and to review water flow around or through the passive hydraulic containment alternative and evaluate impacts to wetlands.	Moderate to low capital costs and no ongoing O&M costs.	**Reject** - based on past site specific history, sheet pile cannot be driven to the depth of the bedrock.
	4b	Slurry Wall	Install a slurry wall by mixing bentonite or other low permeability grout in an excavated trench to stop the flow of water. Alternatively a one-pass trencher could excavate, mix and install bentonite to construct the slurry wall.	**Advantages:** This is a permanent, passive solution. No on-going O&M or annual charges. Relatively simple installation with one-pass or trenching methods. **Disadvantages:** In order for this alternative to be effective, it would have to be constructed between less permeable zones, and tied into the bedrock. Potential impacts to the downgradient wetlands, caused by cutting off flow. Excess COD/BOD could reach wetlands or downgradient receptors.	Potentially Effective - This alternative would be effective if the slurry wall can be tied into the bedrock at depth, and into lower permeability soils at the ends of the slurry wall. Full effectiveness shortly after completion of construction.	Potentially Implementable - Based upon the well logs, depth of bedrock and assumed lower permeability areas to the north and south of the wall. Slurry walls implemented with either one-pass or standard slurry wall construction methods to depths of approximately 30 feet below ground surface are likely attainable at this site.	(See Alternative 4a)	Moderate to low capital costs and no ongoing O&M costs	**Retain** for further analysis.
	4c	Grout Injection	Inject low permeability grout into the subsurface to prevent groundwater migration. Grout injection will seal the void-space in essence stopping groundwater flow through the area of interest.	**Advantages:** This is a permanent, passive solution. No on-going O&M or annual charges. Grout injection method calls for upgradient and downgradient water monitoring to verify effectiveness. **Disadvantages:** In order for this alternative to be effective, it would have to be constructed between less permeable zones, and tied into the bedrock. Potential impacts to the downgradient wetlands, caused by cutting off flow.	Potentially Effective - This alternative would be effective if grout injections can be tied into the bedrock at depth, and into lower permeability soils at the ends of the slurry wall. Full effectiveness shortly after completion of construction.	Potentially Implementable - Grout injections to depths of approximately 30 feet can be constructed.	(See Alternative 4a)	Moderate to high capital costs and no ongoing O&M costs	**Retain** for further analysis.
Hydraulic Containment - Hybrid	5	Wells and pumps with slurry wall.	This alternative is a combination of Alternatives 3b and 4b.	**Advantages:** This is a permanent, combined active and passive solution. Potential advantages over individual installations of Alternatives 3b and 4b would potentially be lower pumping rates, minimizing downgradient wetland impacts, and improved overall effectiveness in attaining sulfate reduction goals at the property line. This alternative has a greater likelihood of maintaining effectiveness during extended electrical or pump failures. **Disadvantages:** Installation costs would be higher than stand alone Alternatives 3b and 4b.	Potentially Effective - This alternative has high likelihood of being successful at preventing sulfate affected water from leaving the property when the system is operational and potentially extends the effectiveness during down-time. Wetland impacts and hydrogeology need to be further defined to ensure effectiveness. Full effectiveness shortly after completion of construction.	Potentially Implementable - See alternatives 3b and 4b.	(See Alternatives 3b and 4b)	Moderate to high capital costs and moderate annual O&M costs.	**Retain** for further analysis.

Remedial Action	Alternative No.	Technology	Description	Advantages or Disadvantages	Screening				Conclusion
					Effectiveness	Implementability	Data Gaps/Data Collection Requirements	Cost	
Sulfate Reduction - In-Situ Biochemical Reduction	6a	Excavate and place in trench	Excavate a trench and mix in granular iron, mulch or other substrates to reduce sulfate as it passes through the permeable reactive barrier (PRB).	**Advantages:** This is a semi-passive solution. O&M requirements may include periodic substrate injections or amendments to ensure effectiveness. Hydrologic impacts to wetlands are not likely. **Disadvantages:** Potential periodic substrate amendment or injections. The PRB may clog over time, or preferential flow paths may be generated that allow sulfate affected water to flow through the PRB without treatment. Risk of water quality issues (high COD/BOD, low DO, etc.) impacting downgradient wetlands or other receptors. Amendments or zero valent iron are potentially high cost.	Potentially Effective - This alternative can be successful if the hydrogeology and geochemistry are well understood and suitable for substrate compatibility. The effectiveness of this alternative would not be immediate, but would take time (several months) to stimulate sulfate reducing bacteria growth. Monitoring and management of electron donor material is required to ensure sufficient sulfate reduction to meet water quality goals at the property line without causing other water quality issues.	Potentially Implementable - Trenches can be constructed to depths of 30 feet below ground surface using various one-pass, traditional, or large diameter drilling techniques. Substrate material replenishment would require periodic injections, excavation, or additional soil mixing.	Hydrogeology and geochemistry has to be fully understood. Higher resolution data on depth of bedrock and soil materials, both in the target flow zone and in surrounding upland units. Bench-scale study and testing to evaluate this alternative and define sulfate reduction rates. Bench or pilot scale study to assist design parameters and evaluate type and longevity of PRB media (iron, mulch, other).	Moderate to high capital costs and moderate O&M costs.	Retain for further analysis.
	6b	In Situ Injection of EHC: permanent wells	Install a line of wells, or multiple lines of permanent wells. Inject EHC or other carbon substrate (possibly with zero valent iron) into the permanent wells. Wells will have to be installed within the radius of influence of injected material. Injection of substrate would occur regularly on a set schedule or based upon monitoring and depletion of hydrogen donor material	**Advantages:** This can either be a semi-passive or active solution. O&M requirements may include constant dosing or periodic injection of amendments to ensure effectiveness. Can set dosing rates to match calculated electron donor need and reduces risk of water quality issues impacting the wetlands. Hydrologic impacts to wetlands are not likely. Potential for low-cost locally available waste material to be used as electron donor substrate. **Disadvantages:** On-going substrate dosing or injections. Permanent wells may clog and require on-going maintenance to ensure that substrate injection would be injectable. Radius of influence testing would be required to design well spacing, but subsequent injections may not attain the same radius of influence. Vertical distribution of injected materials more difficult than alternative 6c.	(See Alternative 6a)	Potentially Implementable - Well spacing can be designed to meet requirements. Injection wells can be constructed to depths up to 30 feet bgs. Substrate material replenishment is easily achieved with permanent wells.	Hydrogeology and geochemistry has to be fully understood. Bench-scale study and testing to evaluate this alternative and define sulfate reduction rates, evaluate type and longevity of electron donor substrate. Pilot scale testing to evaluate well spacing and injection methods to ensure complete vertical and horizontal dispersion of carbon substrate.	Moderate capital costs and moderate to high O&M costs.	Retain for further analysis.
	6c	In Situ Injection of EHC: temporary well points	Same as above, only injection would occur from temporary well points advanced every time an injection is conducted. These points would not be re-used, and subsequent injections would require full drill-rig mobilizations.	**Advantages:** This is a semi-passive solution. O&M requirements include periodic substrate injections or amendments to ensure effectiveness. Hydrologic impacts to wetlands are not likely. **Disadvantages:** On-going substrate amendment or injections. O&M costs are higher than 6b due to mobilization of drilling equipment. Radius of influence testing would be required to design injection point spacing. Risk of water quality issues (high COD/BOD, low DO, etc.) impacting downgradient wetlands or other receptors if injection volumes are too high or low. Amendments are potentially high cost.	(See Alternative 6a)	Potentially Implementable - Injection spacing can be designed to meet requirements. Injection points can be advanced to depths up to 30 feet bgs. Substrate material replenishment would require additional mobilizations.	Hydrogeology and geochemistry has to be fully understood. Bench-scale study and testing to evaluate this alternative and define sulfate reduction rates, evaluate type and longevity of electron donor substrate. Pilot scale testing to evaluate well spacing and injection methods to ensure complete vertical and horizontal dispersion of carbon substrate.	Moderate initial capital costs and moderate to high O&M costs.	Retain for further analysis.

Remedial Action	Alternative No.	Technology	Description	Advantages or Disadvantages	Screening				Conclusion
					Effectiveness	Implementability	Data Gaps/Data Collection Requirements	Cost	
Sulfate Reduction - Active Hydraulic Containment with Ex-Situ Treatment	7a	Reverse Osmosis Treatment System	Install a reverse osmosis water treatment system in conjunction with alternative 3a or 3b to treat extracted water.	**Advantages:** This alternative has the same advantages as alternative 3a or 3b with the additional advantage of treating water. **Disadvantages:** RO systems can be maintenance intensive and have a high capital and operation and maintenance costs. RO treatment systems, especially those with crystallizers are energy intensive. Wastes must be disposed off-site.	Potentially Effective - This has the same effectiveness as alternative 3a or 3b with regard to attaining sulfate goals at the property line	Potentially Implementable - Implementation of the wells and pumps would be the same as alternative 3a or 3b. Additional piping and pumps would be required to move extracted water to the RO treatment plan. Land for siting an RO plant near the extraction wells would require land and a suitable building.	Higher resolution data on depth of bedrock and soil materials. Groundwater flow model to evaluate effectiveness and simulate pumping conditions, evaluate sulfate concentrations at the property line under multiple pumping rates, and evaluate impacts to wetlands. A bench-scale study may be necessary to understand RO treatment effectiveness at sulfate removal	High capital costs and High annual O&M costs.	**Retain** for further analysis (by others).
	7b	Ion Exchange Treatment System	Install an ion exchange water treatment system in conjunction with alternative 3a or 3b to treat extracted water.	**Advantages:** This alternative has the same advantages as alternative 3a or 3b with the additional advantage of treating water. **Disadvantages:** Ion Exchange systems can be maintenance intensive and have a high capital and operation and maintenance costs. Reject waste disposal would be required.	Potentially Effective - This has the same effectiveness as alternative 3a or 3b with regard to attaining sulfate goals at the property line	Potentially Implementable - Implementation of the wells and pumps would be the same as alternative 3a or 3b. Additional piping and pumps would be required to move extracted water to the IX treatment plan. Land for siting an IX plant near the extraction wells would require land and a suitable building.	Higher resolution data on depth of bedrock and soil materials. Groundwater flow model to evaluate effectiveness and simulate pumping conditions, evaluate sulfate concentrations at the property line under multiple pumping rates, and evaluate impacts to wetlands. A bench-scale study may be necessary to understand IX performance with regard to sulfate removal.	High capital costs and High annual O&M costs.	**Retain** for further analysis.

Appendix B

Sulfate Reduction Overview

Sulfate Reduction Overview

Introduction

Sulfur is an essential element for life on earth. It is present throughout most of the earth's crust at a reported average concentration of approximately 500 mg/Kg (Ehrlich, 1981). The fate of sulfur in the environment has been studied extensively (Howarth and Stewart, 1992), due to its potential interactions with many other elements in soil, sediments, aqueous solutions, and the atmosphere. In the environment, sulfur can exist in up to four different oxidation states. These oxidation states are shown in Table 1, ranging from sulfide (the most reduced form with a formal charge of -2 on S) to sulfate (the most oxidized form with a formal charge of +6 on S). The oxidation state and the chemical speciation of sulfur depend on the redox state (degree of oxygenation), pH, microbial activity, and temperature of the environment. Both oxidized and reduced sulfur are reactive following biotic and abiotic pathways. In general, the oxidation of sulfur (from sulfide to sulfate) produces acidity while the reduction of sulfur (sulfate to sulfide) consumes acidity and, in the case of biologically mediated reduction, produces excess alkalinity. Thus, the presence of sulfur, with or without oxygen, has a potentially significant impact on the pH and the overall quality of a water body.

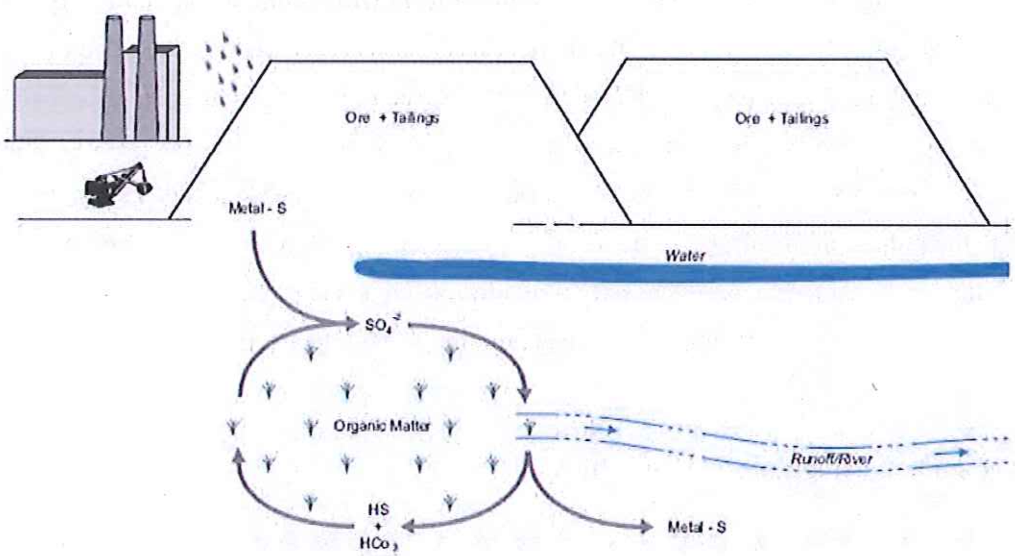
Table B-1. Common oxidation states of sulfur.

Species	Oxidation state (formal charge on S)
HS^-	-2
S (elemental sulfur)	0
S_2O_3	+2
SO_3^{2-}	+4
SO_4^{2-}	+6

Sulfur in Northern Minnesota

In the northern Minnesota mining region, the Biwabik Iron Formation (BIF) contains iron primarily in the form of metal oxides. However, portions of the waste rock in this formation have been documented to contain iron sulfides as well as mixed iron, calcium, and magnesium carbonates. When these ores are mined, the exposure to air and water results in oxidation of the sulfides to sulfate. Depending on the local geochemistry, this oxidation process could result in acid generation. However, because the BIF also contains carbonates, this acid is generally neutralized while releasing bicarbonate and additional iron, calcium, and magnesium into solution. Because iron in the oxidized form is generally insoluble (and precipitates as iron oxide) this sequence of reactions generally results in waters exposed to these rocks being dominated by dissolved sulfate, hardness, and alkalinity. A general conceptual model is shown in Figure B-1, below.

Figure B-1 Sulfur Transformation in the Environment



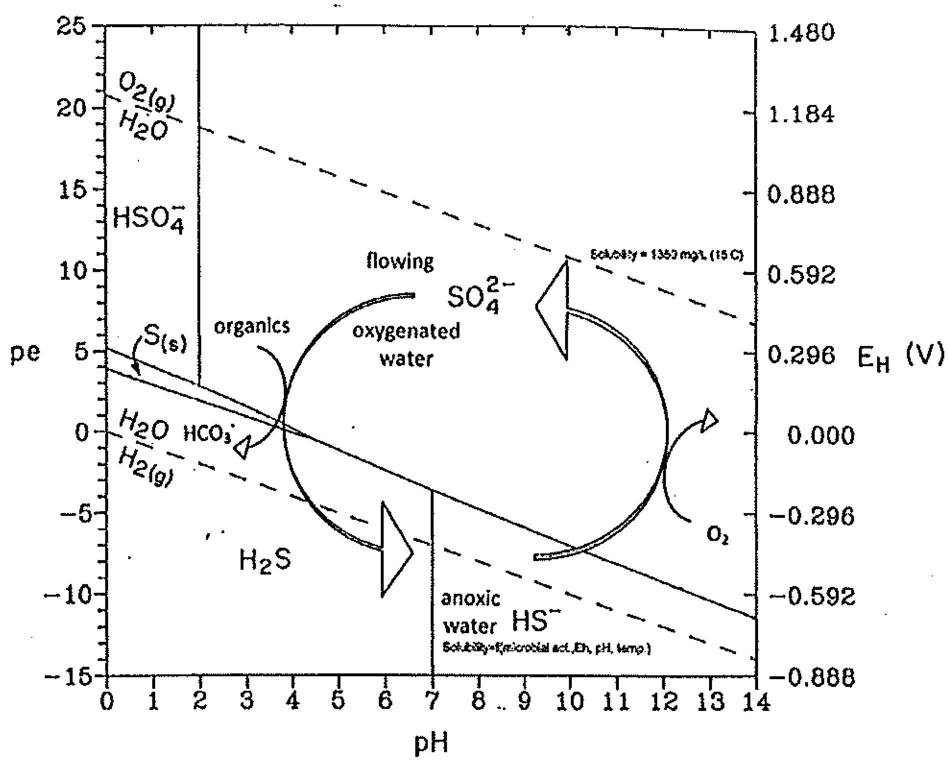
Oxidation States and Solubility of Sulfur Affect Water Treatment Options

Of the oxidation states presented in Table B-1, two are of particular importance in the treatment of sulfate-laden water: sulfide (mainly HS^-) and sulfate (SO_4^{2-}). These oxidation states of sulfur are the most commonly present forms in treatment processes. The speciation of sulfide and sulfate are both pH-dependent, as is illustrated by Figures B-1 and B-2. Because of the range of pH found in northern Minnesota waters (circumneutral to slightly basic), the forms HS^- and SO_4^{2-} are dominant. The Eh-pH diagram for the sulfide-sulfate redox pair is shown in Figure B-2. Sulfide, at low pH, is present as the weak acid, hydrogen sulfide (H_2S). This species has low water solubility (Stumm and Morgan, 1981) and has potential to off-gas. It is also corrosive to many metals, highly toxic, and is a common cause of odor complaints in situations such as municipal sewer systems, treatment plants, and livestock manure. Hydrogen sulfide is the predominant species from pH 1 to 7. From pH 7 to 13, HS^-

dominates, and at pH greater than 13, S^{2-} (sulfide) is the dominant form. In the reduced form, sulfide will readily combine with metal cations to form insoluble compounds.

In the oxidized form of sulfate, solubility varies in relation to the form of cation present, with solubility generally decreasing as the atomic size of the cation increases. Sodium, magnesium and potassium sulfate are all highly soluble and can result in dissolved sulfate concentrations of several thousand milligrams per liter. Calcium sulfate (gypsum) has a moderate solubility, while barium sulfate is generally insoluble.

Figure B-2. Eh – pH diagram of sulfate – sulfide system, only.



Transformation Processes for Sulfate Removal

To remove sulfate from water without causing odor or safety hazards, it must be transformed to an insoluble species that can be physically separated from the water. Most commonly, this is accomplished by the precipitation of calcium or barium sulfate or transformation to the reduced form for precipitation as a metal sulfide. The degree of sulfate or sulfide removal that can be accomplished using chemical precipitation is limited by the solubility of the precipitated species and requires a favorable pH and stoichiometrically sufficient concentration of cation to avoid rate limitations.

Transformations of sulfur from sulfate to sulfide (and back to sulfate) occur in biologically mediated reactions and in some cases can be accomplished abiotically in the environment or within water treatment systems as described in the following sections.

Microbial Transformations

A large number of microbial reduction and oxidation pathways transform sulfur. The general transformation pathways are shown on Figures B-1 and B-2. A detailed review of the bacterial sulfur cycle is provided by Tang et al. (2009). Microbial reduction of sulfate and oxidation of sulfide will readily occur in aquatic environments and boreal forested landscapes. Because both sulfate and sulfide easily undergo redox reactions, securing a stable end-product to precipitate and remove sulfur from aquatic environments may require additional control (for example to minimize water level fluctuations) or methods to actively remove solid phase sulfur species after they have precipitated.

Biologically mediated sulfate reduction can occur via two primary mechanisms: dissimilatory sulfate reduction by heterotrophic microorganisms or autotrophic sulfate reduction by chemolithotrophic microorganisms. In general, these two reactions can be summarized as follows:

- $SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^-$ – for heterotrophic reduction, and
- $SO_4^{2-} + H^+ + 2H_2 \rightarrow HS^- + 2H_2O$ – for autotrophic reduction.

To achieve heterotrophic sulfate reduction, organic matter (manure, emulsified vegetable oil, lactate, saw-dust, wood-chips, straw, peat, etc.) is added to the target matrix. Similarly, to achieve autotrophic sulfate reduction, a source of hydrogen must be added to the subsurface. The most commonly used source for hydrogen addition is zero valent iron (ZVI), where the corrosion of ZVI generates hydrogen by the following reaction:

- $Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$.

Chemical Transformations

Sulfide can be oxidized by exposure to the oxygen in air and water to form sulfate. Reduced sulfur compounds can also be oxidized by the following compounds:

- Hydrogen peroxide
- Chlorine gas
- Hypochlorite
- Chlorine dioxide
- Ozone
- Potassium permanganate

Abiotic sulfate reduction to sulfide is not energetically favorable, as the sulfate ion is very stable and unreactive. This process is employed in the petroleum industry and in the treatment of sulfate-laden water, but requires the input of large amounts of energy in the form of heat.

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U. S. Steel Minntac

Groundwater Monitoring Well MW12

Item 10 - Summary of Monitoring Results: April 2012 - May 2014

Date	Piezometer[1]	Sulfate mg/L	Notes
4/10/2012	PZ12S	577	
	PZ12I	564	
	PZ12D	466	
	PZ12D	461	Duplicate
	Field Blank	<2.5	
5/7/2012	PZ12S	562	
	PZ12I	545	
	PZ12I	537	Duplicate
	PZ12D	460	

[1]PZ12S, PZ12I and PZ12D refer to nested piezometers that were screened, in relative terms, shallow, intermediate and deep, respectively.

Date[1]	Sulfate mg/L	Chloride mg/L	TDS mg/L	pH S.U.	Temperature °C	Specific Conductance µS/cm	Water Surface Elevation ft msl[2]
5/15/2012	476						
7/26/2012	457	98.8	980	6.7	18.2	1244	1454.2
10/25/2012	480	102	899	6.7	8.5	1247	1453.8
5/31/2013	385	82.3	869	6.2	5.8	1418	1454.4
7/30/2013	435	94.9	840	6.9	13.9	1259	1453.8
10/8/2013	444	96.9	857	6.6	9.7	1309	1453.5
5/29/2014	370	82.9	884	6.7	6.0	1317	1454.3

[1]Following the initial two rounds of sampling from the nested piezometers, all sampling and analysis has been from PZ12D, now considered to be Monitoring Well 12 (MW12).

[2]msl = mean sea level.